Enthalpy Change $(\Delta \mathrm{H})$ : is the heat change at constant pressure. Usually quoted in $\mathrm{KJ} / \mathrm{mol}$.

| Exothermic <br> Reaction | $\Delta H=-v e$ | Releases heat energy from system to surroundings. <br> Temperature of surroundings increases. | $\mathrm{C}_{5} \mathrm{H}_{12}+8 \mathrm{O}_{2}------>5 \mathrm{CO}_{2}+6 \mathrm{H}_{2} \mathrm{O}$ |  |
| :---: | :---: | :---: | :---: | :---: |
| Endothermic <br> Reaction | $\Delta \mathrm{H}=+\mathrm{ve}$ | Takes in heat energy from surroundings to system. <br> Temperature of surroundings decreases. | $\mathrm{CaCO}_{3}-------->\mathrm{CaO}+\mathrm{CO}_{2}$ |  |

## Key Definitions

Standard Enthalpy change of Formation $\left(\Delta H_{f} \Theta\right)$ : is the enthalpy change when one mole of a substance is formed from its constituent elements under standard conditions, with all reactants and products in their standard states

$$
\begin{aligned}
& N a_{(s)}+\frac{1}{2} \mathrm{Cl}_{2(g)}---\rightarrow \mathrm{NaCl}_{(s)} \\
& 2 N a_{(s)}+\mathrm{Cl}_{2(g)}----\rightarrow 2 \mathrm{NaCl}_{(s)} \quad \text { incorrect as not one mole formed as per definition. }
\end{aligned}
$$

Standard Enthalpy change of Combustion $\left(\Delta \mathrm{H}_{\mathrm{c}} \ominus\right)$ : is the enthalpy change when one mole of substance is completely burned/combusted in oxygen under standard conditions, with all reactants and products in their standard states

$$
\mathrm{C}_{3} \mathrm{H}_{8_{(g)}}+5 \mathrm{O}_{2_{(g)}}----\rightarrow 3 \mathrm{CO}_{2_{(g)}}+4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

## Note:

Standard enthalpy of formation of elements is $0 \mathrm{KJ} / \mathrm{mol}$ e.g. $\mathrm{Mg}, \mathrm{O}_{2}$
Standard enthalpy of combustion of Oxygen is $0 \mathrm{KJ} / \mathrm{mol}$.
Standard conditions $(\ominus)$ refer to Temperature: 298 K , Pressure: 100 kPa

## Calculating Enthalpy change of a reaction

The enthalpy change of a reaction can be calculated in the following ways where applicable:

1) Hess's Law
2) Calorimetry
3) Mean Bond Enthalpies

## Hess' Law

Hess's Law states that the enthalpy change of a reaction is independent of the route taken.

$\Delta \mathrm{H}_{\mathrm{r}}=\Delta \mathrm{H}_{1}+\Delta \mathrm{H}_{2}$


## Example 1

Calculate the standard enthalpy change of the combustion of Propane, given the following data:
$\Delta \mathrm{H}_{\mathrm{f}}\left[\mathrm{C}_{3} \mathrm{H}_{8}\right]=-104.7 \mathrm{KJ} / \mathrm{mol}$

$$
\begin{gathered}
\Delta \mathrm{H}_{\mathrm{f}}\left[\mathrm{CO}_{2}\right]=-393.5 \mathrm{KJ} / \mathrm{mol} \\
C_{3} H_{8_{(g)}}+5 \mathrm{O}_{2_{(g)}}-------\rightarrow 3 \mathrm{H}_{\mathrm{f}}\left[\mathrm{H}_{2} \mathrm{O}\right]=-285.8 \mathrm{KJ} / \mathrm{mol} \\
2 \mathrm{C}_{(\mathrm{s})}+4 \mathrm{H}_{2(\mathrm{~g})}+5 \mathrm{O}_{2} \mathrm{O}_{(\mathrm{g})} \\
\Delta \mathrm{H}_{\mathrm{r}}=104.7+-2323.7=-2,219 \mathrm{KJ} / \mathrm{mol}
\end{gathered}
$$

Note: The question states to calculate the enthalpy change of combustion of Propane. This does not mean we use a combustion system. The system we use depends on the enthalpy values provided. In this case we are provided with enthalpy of formation values, hence use a formation system.

## Example 2

Calculate the standard enthalpy change of the formation of $\mathrm{C}_{7} \mathrm{H}_{8}$ given the following data:
$\Delta \mathrm{H}_{\mathrm{c}}[\mathrm{C}]=-393 \mathrm{KJ} / \mathrm{mol}$
$\Delta \mathrm{H}_{\mathrm{c}}\left[\mathrm{H}_{2}\right]=-286 \mathrm{KJ} / \mathrm{mol}$
$\Delta \mathrm{H}_{\mathrm{c}}\left[\mathrm{C}_{7} \mathrm{H}_{8}\right]=-3907 \mathrm{KJ} / \mathrm{mol}$


$$
\Delta \mathrm{H}_{\mathrm{r}}=-3,895++3,907=+12 \mathrm{KJ} / \mathrm{mol}
$$

Note: The question states to calculate the enthalpy of formation of Methylbenzene $\left(\mathrm{C}_{7} \mathrm{H}_{8}\right)$, but we use a combustion Hess' law system as the values provided are standard enthalpy of combustion values. Also, note the combustion products in this case are Carbon dioxide and Water.

## Key Notes

In certain cases, the enthalpy changes of combustion/formation will be given to you in the form of an equation i.e. you have to be able to identify whether this is $\Delta \mathrm{H}_{\mathrm{f}}$ or $\Delta \mathrm{H}_{\mathrm{c}}$. In some cases, a reaction can represent both an enthalpy of formation of one substance, but enthalpy of combustion of another. Let's look at a few examples:

| Reaction Equation | Standard Enthalpy of Formation? | Standard Enthalpy of Combustion? |
| :---: | :---: | :---: |
| $C_{(s)}+\frac{1}{2} O_{2_{(g)}}-----\rightarrow \mathrm{CO}_{2_{(g)}}$ | YES- This equation represents the formation of one mol of Carbon dioxide from its constituent elements. | YES- This equation also represents the complete combustion of Carbon as one mole is completely burned/combusted. |
| $\mathrm{H}_{2(g)}+\frac{1}{2} \mathrm{O}_{2_{(g)}}-----\rightarrow \mathrm{H}_{2} \mathrm{O}_{(l)}$ | YES- This equation represents the formation of one mol of Water from its constituent elements. | YES- This equation also represents the complete combustion of Hydrogen as one mole is completely burned/combusted. |
| $\mathrm{N}_{2(\mathrm{~g})}+2 \mathrm{O}_{2_{(g)}}-----\rightarrow 2 \mathrm{NO}_{2_{(g)}}$ | NO- Does not represent the enthalpy of formation of Nitrogen dioxide, as 2 moles are formed. | YES- This equation also represents the complete combustion of Nitrogen as one mole is completely burned/combusted. |

## Calorimetry

The Enthalpy change of a reaction can also be calculated experimentally via calorimetry. The general equation used to calculate the energy change is:

$$
Q=m \times \mathrm{c} \times \Delta \mathrm{T}
$$

Where:
$Q=$ heat change ( $J$ )
$\mathrm{m}=$ mass of substance being heated or cooled (g)
$\mathrm{c}=$ specific heat capacity $\left(\mathrm{Jg}^{-1} \mathrm{~K}^{-1}\right)$ : states the energy required to raise the temperature of 1 g of a substance by 1 K .
$\Delta \mathrm{T}=$ temperature change (K)
In order to calculate enthalpy change, recall units are $\mathrm{KJ} / \mathrm{mol}$, we divide Q by mol. Ensure to convert Q from Joules to KJ by dividing by 1000 .

$$
\Delta \mathrm{H}=\frac{\mathrm{Q}}{\mathrm{n}}=\frac{K J}{m o l}
$$

## Calculating enthalpy of combustion

A fuel can be burned in order to heat a pre-determined mass of water to calculate the enthalpy change of combustion of the fuel.

## Example 3

4.6 of Ethanol was completely burned to raise the temperature of $100 \mathrm{~cm}^{3}$ of Water from $20^{\circ} \mathrm{C}$ to $28^{\circ}$. Calculate the enthalpy change of combustion?

First calculate the heat change:

$$
\begin{gathered}
Q=m \times \mathrm{c} \times \Delta \mathrm{T} \\
Q=100 \times 4.18 \times 8 \\
Q=3,344 \mathrm{~J}=3.344 \mathrm{KJ}
\end{gathered}
$$

In order to calculate the energy released per mole, we need to calculate the moles of ethanol:

$$
n=\frac{\operatorname{mass}(g)}{M r}=\frac{4.6}{46}=0.1 \mathrm{moles}
$$

The enthalpy change of combustion in $\mathrm{KJ} / \mathrm{mol}$ can be calculated as follows:

$$
\Delta \mathrm{H}=\frac{\mathrm{Q}}{\mathrm{n}}=\frac{3.344}{0.1}=-33.44 \mathrm{KJ} / \mathrm{mol}
$$

Note, a negative sign is included in the answer, as combustion is an exothermic reaction i.e. temperature of the surrounding (water) goes up.
Discrepancies in this method include: incomplete combustion of fuel, heat loss, evaporation of fuel post weighing, non-standard conditions.

Example 4-Calculating enthalpy change of neutralisation reactions
$30 \mathrm{~cm}^{3}$ of $0.6 \mathrm{~mol} / \mathrm{dm}^{3} \mathrm{HCl}$ was added to $20 \mathrm{~cm}^{3}$ of $0.5 \mathrm{~mol} / \mathrm{dm}^{3}$ of KOH . The temperature of the solution increased from $20^{\circ} \mathrm{C}$ to $27.2^{\circ} \mathrm{C}$. Calculate the enthalpy change of the reaction:

First calculate the heat change:

$$
\begin{gathered}
Q=m \times \mathrm{c} \times \Delta \mathrm{T} \\
Q=50 \times 4.18 \times 7.2 \\
Q=1,504.8 \mathrm{~J}=1.5048 \mathrm{KJ}
\end{gathered}
$$

In order to calculate the energy released per mole, we need to calculate the moles of HCl and KOH , to identify which is the limiting reactant.

$$
\text { moles of } \mathrm{HCl}=\frac{c \times \mathrm{xV}\left(\mathrm{~cm}^{3}\right)}{1000}=\frac{0.6 \times 30}{1000}=0.018 \text { moles } \quad \text { moles of } \mathrm{KOH}=\frac{c \times \mathrm{x}\left(\mathrm{~cm}^{3}\right)}{1000}=\frac{0.5 \times 20}{1000}=0.010 \text { moles }
$$

Note only the limiting reactant contributes to the energy change, the excess mol do not react hence do not contribute to energy change. Therefore, the limiting reactant moles should be used. Note temperature of the solution increases, hence exothermic:

$$
\Delta \mathrm{H}=\frac{\mathrm{Q}}{\mathrm{n}}=\frac{1.5048}{0.01}=-150.48 \mathrm{KJ} / \mathrm{mol}
$$

## Example 5- Calculating enthalpy change of displacement reactions

5 g of Zn is added to $25 \mathrm{~cm}^{3}$ of $0.6 \mathrm{~mol} / \mathrm{dm}^{3} \mathrm{CuSO}_{4}$ soln. The temperature of the solution increases by 5.5 K . Calculate the enthalpy change of the reaction?
First calculate the heat change:

$$
\begin{gathered}
Q=m \times \mathrm{c} \times \Delta \mathrm{T} \\
Q=25 \times 4.18 \times 5.5=574.5 \mathrm{~J}=0.575 \mathrm{KJ}
\end{gathered}
$$

In order to calculate the energy released per mole, we need to calculate the moles of Zn and $\mathrm{CuSO}_{4}$, to identify which is the limiting reactant.

$$
\text { moles of } Z n=\frac{\operatorname{mass}(g)}{A r}=\frac{5}{65.4}=0.0765 \text { moles } \quad \text { moles of } \text { CuSO }_{4}=\frac{c \times V\left(\mathrm{~cm}^{3}\right)}{1000}=\frac{0.6 \times 25}{1000}=0.015 \text { moles }
$$

Note only the limiting reactant contributes to the energy change, the excess mol do not react hence do not contribute to energy change. Therefore, the limiting reactant moles should be used:

$$
\Delta \mathrm{H}=\frac{\mathrm{Q}}{\mathrm{n}}=\frac{0.575}{0.015}=-38.3 \mathrm{KJ} / \mathrm{mol}
$$

## Bond Enthalpies

Bond Dissociation Enthalpy : is the enthalpy change required to break one mol of a covalent bond with all species in their gaseous state.
Mean Bond Enthalpy: average value of the bond dissociation enthalpy for a given bond taken from a range of different compounds.

$$
C l_{2_{(g)}}-----\rightarrow 2 \mathrm{Cl}_{(g)} \quad \Delta H=242 \mathrm{KJ} / \mathrm{mol}
$$

Note: Bond enthalpy values are always positive, as energy is required to break the bond. Bond Breaking= endothermic. Bond forming= exothermic.

To calculate enthalpy change of a reaction using bond enthalpies, use the below formulae

$$
\Delta H=\sum \text { Bonds energies of bonds broken }-\sum \text { Bonds energies of bonds formed }
$$

## Example 6

Calculate the enthalpy change of combustion of Pentane using the data table provided below?

| Bond | C-C | C-H | O=O | C=O | O-H |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Mean Bond Enthalpy KJ/mol | 347 | 412 | 497 | 744 |  |



$$
\begin{aligned}
& \text { C-H : } 12 \times 412=4,944 \\
& \text { C-C }: 4 \times 347=1,388 \\
& \mathrm{O}=\mathrm{O}: 8 \times 497=3,976 \\
& =10,308
\end{aligned}
$$

$$
\begin{aligned}
& \mathrm{C}=\mathrm{O}: 5 \times 2 \times 744=7,440 \\
& \mathrm{O}-\mathrm{H}: 6 \times 2 \times 463=5,556 \\
& =12,996
\end{aligned}
$$

$$
\begin{gathered}
\Delta H=\sum \text { Bonds energies of bonds broken }-\sum \text { Bonds energies of bonds formed } \\
\Delta H=10,308-12,996=-2,688 \mathrm{KJ} / \mathrm{mol}
\end{gathered}
$$

Note: Drawing a displayed formula of the reactants and products helps with visualisation of the no. of bonds present in the respective reactants and products. Highly recommend this.

